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Post-mortem analysis of a 5-cell HT-PEMFC stack under the effect of induced starvation of reactant gases

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1. Introduction

Membrane electrode assemblies (MEAs) are one of the most critical and expensive components of a PEM fuel cell [1]. For this reason, their durability and robustness are issues attracting a great deal of attention in the literature [2]. Pt catalysts, usually employed on PEM fuel cells, are the most active for the reactions taking place in the cell. However, these catalysts are usually supported on a carbonaceous material, which is prone to corrosion. During the operation of a fuel cell, several mechanisms occur, leading to the degradation of the catalytic layers and the membrane [2]. Reactants starvation has been recognized as one of the phenomena causing a greater MEA degradation [3]. When hydrogen (at the anode) or oxygen (at the cathode) are not sufficiently or correctly supplied, the cell potential can reverse, reaching highly corrosive potentials (mainly at the anode). When this occurs, reactions such as water electrolysis and carbon oxidation can take place in the electrodes, leading to Pt dissolution and agglomeration. Besides, cell voltage reversal events can lead to significant heat generation, creating pin-holes in the membrane and eventually a short-circuit [4]. It is generally believed that when a cell suffers voltage reversal in a stack; the neighboring cells follow the same trend [4]. Several studies have been conducted on low temperature PEM fuel cells (LT-PEMFCs) [5]. However, there is not much research on starvation tests on high-temperature PEM fuel cell (HT-PEMFCs) stacks. HT-PEMFCs differ from their low-temperature counterparts on the temperature of operation, being around 120-200ºC. The present research aims to analyze the effect of induced starvation on the physical-chemical features of high-temperature MEAs. A specially designed 5-cell stack was operated under starvation conditions. Two types of tests were performed acting on the central cell (number 3). Tests were denoted as moderate and severe starvation, respectively. The difference between them depended on the intensity of the limitation imposed to the gases flowrate. MEAs from each cell (from 1 to 5) were analyzed after the tests by transmission and scanning electron microscopy, and by X-ray diffraction in order to determine the extent of degradation caused by starvation on one cell.

2. Experimental

2.1 Stack description and starvation tests

The experiments were performed using a specifically designed 5-cell stack, which enables controlled variations of the gases supplied to any of its individual cells. Commercial G1018 Dapozol® 100 high-temperature MEAs, manufactured by Danish Power System® (DPS) were used. The stack central cell (cell 3) was subjected to different degrees of reactant gases deprivation. Two different tests were performed, which are identified as “moderate”, and “severe” starvation. In the “moderate starvation” case, the flowrate to cell 3 was limited to 80% of that corresponding to stoichiometric flow conditions for the demanded current of 32.7 A. The total duration of the test was almost 2 hours, but the time during which cell 3 remained under gas starvation was 30 minutes. For the "severe starvation" tests, the flowrate of reactant gases was reduced until 50% in 10% steps. The cell operated for 15 minutes in each one of these steps. In the final condition (50% of the flow) the cell was maintained in operation for 30 minutes, and after this time the flowrate of both gases was set again to 100%. It is to be noted note that the “severe starvation” tests were performed after the “moderate starvation” one.

2.2 Physical and chemical characterization

MEAs were analyzed by different characterization techniques before and after the performance/starvation tests, in order to investigate the effects of starvation on their physical-chemical characteristics. Morphological features of both fresh and used MEAs were observed by analyzing a cross-section with scanning electron microscopy coupled with energy dispersive X-ray spectroscopy. Catalysts grafted from the MEAs prior to the tests and after them were also analyzed by X-Ray diffraction. Crystallite sizes of Pt were calculated from the Scherrer's equation on the (2 2 0) peak. Particle size and morphology of Pt particles on both anode and cathode were investigated with transmission electron microscopy. Samples of water obtained from the stack from both anode and cathode sides were analyzed by atomic emission spectrometry coupled with inductive plasma (ICP-AES). The analysis focused on the determination of the phosphorus and platinum that could be dragged from the MEAs.Some of these results have been omitted here due to space limitations.

3. Results and Discussion

A visual evaluation of the different MEAs was performed once the stack was disassembled. It was confirmed that no evident damages were observed in the MEAs of cells 1, 2, 4 and 5. However, the MEA in cell 3 showed clear damages. As displayed on Fig. 1a), it was verified that on the GDL of the anode side there were some scorched zones indicative of a harmful increase in local temperature. Evidences of the excessive local temperature values reached in the damaged zones are the perforations detected in the GDL of the anode side, as shown in Fig. 1b). On the other hand, orifices were not observed neither in the membrane nor in the GDL of the cathode electrode. The orifices in the GDL suggest that the local temperature reached very high values in the damaged area during the starvation experiments. The non-uniform temperature distribution can be attributed, among other factors, to the high concentration of water in these areas, and the uneven distribution of reactant gases.

a) b)

Figure 1. Damages observed in the elements of the MEA used in cell 3 after starvation tests

Different areas of the MEAs of cells 1, 3, 4 and 5 were studied by SEM-EDX, in order to evaluate their morphological features after operation. These post-mortem studies served to understand the damages caused by the induced reactant gases starvation in cell 3. An unused (fresh) MEA that could serve as a reference to the main conclusions was also analysed (Figure 2a). Fig. 2b, shows a photograph of the MEA of cell 3 after the tests. It can be seen that the damages caused by the starvation experiments are catastrophic. The different layers are clearly separated, and the thickness of the catalyst layer of the anode side has thinned significantly. Furthermore, the polymer of the membrane is calcined, appearing somehow crystallized. These results could be explained by the high local temperatures reached in that area. The delamination between the membrane and the catalytic layers of both electrodes can be also caused by the migration of the H_3PO_4 during the first hours of operation of the stack and by the induced reactant gases starvation in the stack. Acid migration causes a gradual decrease in the pH of water, which could be one of the possible reasons for the increase in the resistance of the charge transfer verified in PEMFCs.

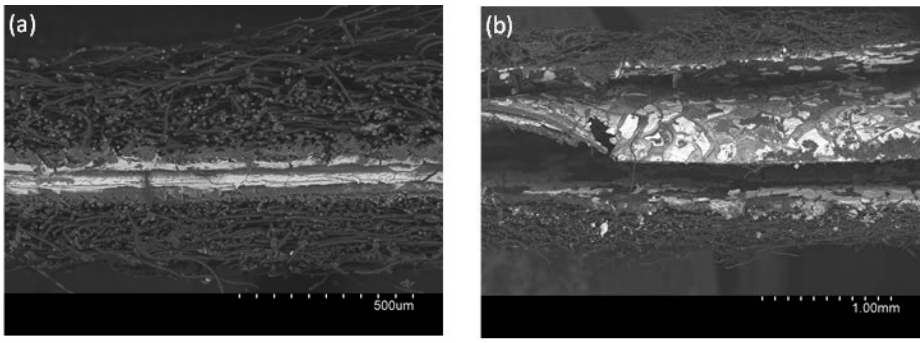

Figure 2. SEM images of cross-sectioned-MEAs for (a) the unused (fresh) MEA and for (b) MEA of cell 3.

Pt catalysts grafted from both the fresh and used MEAs (after the starvation tests) were analyzed by X-Ray diffraction. Crystallite sizes were calculated by the Schrerrer's law. Catalysts in both anode and cathode sides on the fresh MEA (prior to use) presented Pt crystallites around 3.7 nm. All the MEAs see an increase of the Pt crystallite size due to the degradation suffered during operation. In general, the crystallite size for both anodes and cathodes almost doubles after the stack operation, being more evident in the case of the anode (7.5 nm medium crystallite size versus 7.0 nm medium crystallite size for the cathode). The anode from the starved cell, cell 3, presents a great enlargement of the Pt crystallite size: 17 nm (4.6 times the original size), whereas the cathode, keeps the same trend as the other cells (7.6 nm). This confirms that the starvation of hydrogen entails a very aggressive degradation for the catalyst, due to the known water electrolysis and carbon corrosion suffered when potential in the anode rises [12].

4. Conclusions

Visual inspection of the MEA corresponding to the central cell of a 5-cell stack has shown obvious damage after being subjected to an induced gas starvation. It has been verified that on the gas diffusion layer (GDL) of the anode side there were some scorched zones, indicative of a significant increase in local temperature. This hypothesis was also confirmed by the post-mortem analysis performed by SEM-EDX. XRD showed that in general, anodes suffered more degradation than cathodes, in particular, in the starved cell, which presented both a degraded carbon support and a great agglomeration of Pt particles. These results confirm that the starvation of hydrogen causes an aggressive degradation for the catalyst, due to the water electrolysis and carbon corrosion suffered when the potential in the anode rises.

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